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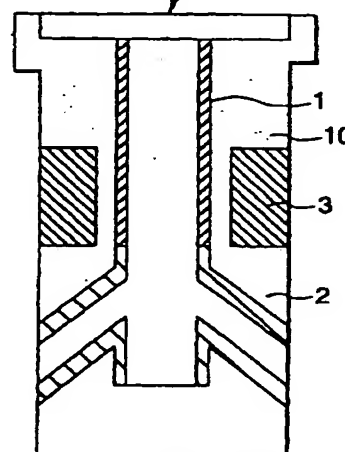
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(54) **IMMERSION NOZZLE FOR CONTINUOUS CASTING OF STEEL**

(57) A submerged nozzle for continuous casting of steel wherein the whole nozzle or a part or the whole of the inner wall portion thereof which comes into contact with molten steel is made of a spinel-periclase-graphite type refractory, especially a spinel-periclase-graphite type refractory comprising 50 to 95% by weight of spinel, 0 to 20% by weight periclase, 5 to 30% by weight of graphite, and not more than 3% by weight of unavoidable impurities.

The inner wall portion 1 and the portion 2 around the spout of the inner wall portion can be made of the above spinel-periclase-graphite type refractory, the nozzle main body can be made of AG-based refractory, and the powder line portion 3 can be made of ZrO<sub>2</sub>-C type refractory.

**FIG. 7****MATERIAL  
ARRANGEMENT  
PATTERN 7**

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## Description

## Technical Field:

[0001] This invention relates to a submerged nozzle for continuous casting of steel which is prevented from clogging and is remarkably prevented from being damaged and secures safe operation with no fear of nozzle cracking. It relates to a submerged nozzle for continuous casting of steel which is suited to not only casting of Al-killed steel but casting of high-oxygen steel, high-Mn steel, Ca-treated steel, stainless steel, etc.

## Background Art:

[0002] In continuous casting of steel,  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -C-based (hereinafter referred to as AG-based) submerged nozzles excellent in spalling resistance have conventionally been used most widely.

[0003] However, when used in casting Al-killed steel, the AG-based nozzles involve the problem of clogging due to deposition of an  $\text{Al}_2\text{O}_3$  inclusion in molten steel. To the contrary, when used for casting high-oxygen steel, high-Mn steel, Ca-treated steel, stainless steel, etc., the problem of nozzle corrosion (melting loss) arises. Clogging and corrosion of a nozzle not only incur a

[0004] reduction of the lifetime of the refractory but hinder steel making operation and give adverse influences to the steel products' quality. Therefore, it is an urgent need to develop a nozzle for continuous casting of steel which possesses resistance to both clogging and corrosion.

[0005] Under these circumstances, JP-A-3-243258 discloses a nozzle having a cylindrical sleeve inserted therein, the sleeve comprising one or a combination of two or more of carbonless materials containing (a) 90% by weight or more of  $\text{Al}_2\text{O}_3$ , (b) 90% by weight or more of  $\text{MgO}$  or (c) 90% by weight or more of  $\text{ZrO}_2$ . However, this nozzle still cannot get rid of the corrosion problem.

[0006] For the purpose of reducing clogging of a nozzle, JP-A-5-237610 proposes using a refractory material comprising less than 1% by weight each of carbon and  $\text{SiO}_2$ , 1 to 40% by weight of spinel, 0.5 to 15% by weight of  $\text{MgO}$ , and the balance of  $\text{Al}_2\text{O}_3$  as an inner layer of a submerged nozzle but does not achieve sufficient effects.

[0007] It is accepted that an AG-based nozzle gets clogged in casting of Al-killed steel chiefly through the following mechanism. At first, the reaction of formula (1) takes place between  $\text{SiO}_2$  and C used as refractory raw materials in high-temperature refractories. Then the produced SiO (gas; hereinafter referred to as (g)) and CO (g) diffuse in the interface between the nozzle and molten steel and react with Al in the molten steel to form an  $\text{Al}_2\text{O}_3$  layer of network form on the hot face of the nozzle as represented by formulae (2) and (3), respectively.

[0008] Structurally, because the network  $\text{Al}_2\text{O}_3$  layer is very coarse, the  $\text{Al}_2\text{O}_3$  inclusion in the molten steel is liable to collide therewith and deposit thereon. As the deposition of  $\text{Al}_2\text{O}_3$  inclusion proceeds, clogging of the nozzle proceeds.



[0009] In the above formulae, (s) represents a solid phase; (g) represents a gas phase; and  $\text{Al}$ ,  $\text{Si}$ , and  $\text{C}$  represent dissolved Al, Si and C, respectively, in molten steel.

[0010] On the other hand, the present inventors' studies on the mechanism of corrosion of AG-based nozzles in casting high-oxygen steel, high-Mn steel, stainless steel, etc. have revealed the following facts.

[0011] At first, carbon in the hot face of refractories dissolves in molten steel as is represented by formula:



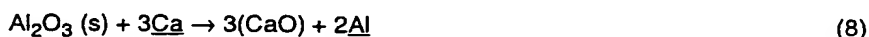
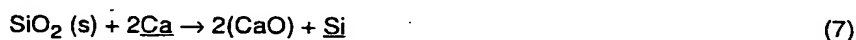
That is, the hot surface is converted into  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  oxides. Thereafter, Mn, O and Fe in molten steel penetrate the hot surface in the form of MnO and FeO as is represented by formulae:



wherein (l) represents a liquid phase; and Mn represents dissolved Mn in molten steel.

[0012] Further, MnO-FeO inclusions in the molten steel collide with and deposit on the hot surface. The MnO and FeO having penetrated by these two causes react with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  on the hot surface to form an  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -MnO-FeO-based liquid slag. The slag runs away together with the flow of molten steel to cause corrosion of the refractory.

[0013] In case of Ca-treated steel, Ca in molten steel reduces  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  on the hot surface to form CaO, which is represented by formulae:



The resulting CaO penetrates into the hot surface. In addition, CaO- $\text{Al}_2\text{O}_3$  inclusions in the molten steel collide with and deposit on the hot surface. As a result, a CaO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ -based liquid slag is generated on the hot surface to cause corrosion of the nozzle refractories.

[0014] The nozzles proposed in JP-A-3-243258 and JP-A-5-237610 have the following disadvantages.

1) In casting Al-killed steel, the reactions of formulae (1) to (3) forming a network  $\text{Al}_2\text{O}_3$  layer hardly occur because the sleeve or the inner layer of the nozzle which comes into contact with molten steel contains substantially no  $\text{SiO}_2$  nor graphite. Therefore, some effects are obtained in suppressing clogging of the nozzle but are not so effective for the following reason. A refractory usually has a porosity of ten and several or more percents. While relatively denser than the network  $\text{Al}_2\text{O}_3$  layer, the pores are still coarse enough to unavoidably cause the  $\text{Al}_2\text{O}_3$  inclusion in molten steel to deposit on the hot surface rapidly.

2) In casting high-oxygen steel, high-Mn steel, Ca-treated steel, stainless steel, etc., the reactions of formulae (5) to (8) take place, and also the inclusions of the molten steel deposit. Therefore, generation of a liquid slag on the hot surface and resultant corrosion of the nozzle refractories unavoidably result.

3) If, on the other hand, such a dense material as ceramics whose porosity is less than several percents is used as a sleeve or an inner layer, there is a fear that the nozzle may be broken during preheating or use due to reduced spalling resistance. That is, where a refractory containing 90% by weight or more of  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  is disposed on the inner side of a nozzle, inclusive of the spout, because such a refractory has a greater expansion coefficient than the AG-based material making up the nozzle main body, the nozzle refractories tend to have deteriorated spalling resistance. In particular, cracks are apt to develop in the vicinity of the spout of the nozzle during use. This is because there are many hot surfaces susceptible to thermal shocks in this portion and also these hot surfaces have such shapes as to allow stresses to concentrate.

[0015] This invention has been made in the light of the above-described problems. It is an object of the present invention to provide a submerged nozzle for continuous casting of steel which has resistance to  $\text{Al}_2\text{O}_3$  deposition, corrosion resistance, and spalling resistance and is suitable for casting not only Al-killed steel but high-oxygen steel, high-Mn steel, Ca-treated steel, stainless steel, and the like.

[0016] Hence, the present inventors have investigated into various kinds of refractories, especially spinel-periclase type refractory and spinel-periclase-graphite type refractory. As a result, they have reached the following findings and completed the present invention.

[0017] The terminologies "spinel-periclase type refractory" and "spinel-periclase-graphite type refractory" as used herein are intended to include those having no periclase.

[0018] In the inside of spinel-periclase-graphite type refractory, the following reaction occurs between MgO of spinel or periclase and graphite in high temperature:



The produced Mg gas and CO gas diffuse in the interface between the refractory and molten steel to form a dense MgO layer on the surface of the refractory through either of the following two reactions:

Reaction 1: Reaction between Mg gas and dissolved oxygen (O) in the molten steel, i.e.,



Reaction 2: Reaction between Mg gas and CO gas, i.e.,



[0019] The MgO layer formed prevents the reactions of formulae (1) to (3) forming a network  $\text{Al}_2\text{O}_3$  layer on the hot surface in casting Al-killed steel. The MgO layer is structurally very dense, having a porosity of approximately zero, so that it hardly causes the  $\text{Al}_2\text{O}_3$  inclusion of molten steel to collide therewith and deposit thereon. That is, the MgO layer suppresses clogging of a nozzle due to deposition of the  $\text{Al}_2\text{O}_3$  inclusion.

[0020] The dense MgO layer also suppresses corrosion of a nozzle by molten steel in casting high-oxygen steel, high-Mn steel, Ca-treated steel, stainless steel, etc. through the following conceivable mechanism.

1) MgO has small reactivity with molten steel and hardly allows MnO and FeO from molten steel to penetrate there-through.

2) Because the MgO-spinel binary system has a very high solidus temperature (2000°C or higher), a liquid slag phase does not generate even if MnO and FeO penetrate.

3) Being so dense, the MgO layer does not allow MnO-FeO inclusions in molten steel to enter the inside of the nozzle.

[0021] Once the dense MgO layer is formed, and the CO partial pressure in the refractory elevates, the reactions of formulae (9) through (11) do not proceed any more.

[0022] Since the MgO layer formed is as thin as several tens of micrometers ( $\mu\text{m}$ ), it gives no adverse influences on the spalling resistance of the nozzle.

[0023]  $\text{Al}_2\text{O}_3$  and MgO in spinel exist in the form of their composite oxides,  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ , and accordingly have reduced thermodynamic activity. Therefore the reactions of formulae (5) to (8) hardly occur. The inventors have also found that periclase does not produce a low-melting liquid slag even if it reacts with elements in molten steel.

[0024] The submerged nozzle for continuous casting of steel according to the present invention has been completed based on these findings.

#### Disclosure of the Invention:

[0025] The submerged nozzle for continuous casting of steel according to the present invention is characterized in that the whole nozzle or a part or the whole of the inner wall portion of the nozzle which comes into contact with molten steel is made of a spinel-periclase-graphite type refractory material.

[0026] The submerged nozzle for continuous casting of steel of the present invention is characterized in that the whole nozzle or a part or the whole of the inner wall portion of the nozzle which comes into contact with molten steel is made of a spinel-periclase-graphite type refractory material comprising 50 to 95% by weight of spinel, 0 to 20% by weight periclase, 5 to 30% by weight of graphite, and not more than 3% by weight of unavoidable impurities.

[0027] The submerged nozzle for continuous casting of steel of the present invention is characterized in that at least a part of the inner wall portion of the nozzle which comes into contact with molten steel is made of a spinel-periclase type refractory material, and at least a part of the portion surrounding the spout is made of a spinel-periclase-graphite type refractory material.

[0028] The submerged nozzle for continuous casting of steel of the present invention is characterized in that at least a part of the inner wall portion of the nozzle which comes into contact with molten steel is made of a spinel-periclase type refractory material, and at least a part of the portion surrounding the spout is made of a spinel-periclase-graphite type refractory material having a graphite content of 5 to 20% by weight.

[0029] The above-described spinel-periclase-graphite type refractories can be used to make the whole nozzle of the present invention or, according to necessity, a part of the nozzle, for example the inner wall portion of the nozzle which comes into contact with molten steel.

[0030] The nozzle having the spinel-periclase-graphite type refractories over all the body or in its inner wall portion including the portion around the spout did not suffer from corrosion, secured spalling resistance, and developed no cracks during use.

[0031] It is also possible to apply spinel refractories or spinel-periclase type refractories to at least part of the inner wall portion of the nozzle other than the portion around the spout and to apply the above-described spinel-periclase-graphite type refractories to at least part of the inner wall portion around the spout.

[0032] When used in casting high-oxygen steel, high-Mn steel, Ca-treated steel, stainless steel, etc., the nozzle having the spinel or spinel-periclase type refractories in the inner wall portion thereof and the spinel-graphite or spinel-periclase-graphite type refractories in the portion around the spout did not suffer from corrosion on its inner wall portion and secured spalling resistance even in the portion around the spout, developing no cracks during use.

[0033] It is desirable to use, as starting materials of the refractories for the nozzle, a spinal raw material and/or a magnesia raw material comprising periclase. In case where a magnesia raw material and an alumina raw material are used simultaneously as starting raw materials, magnesia and alumina react with each other during firing or use of the refractory materials to form spinel. There is a fear that the refractory material expands concurrently with the progress

of this reaction to cause cracks.

[0034] The spinel-periclase-graphite type refractories should have a graphite content of 5 to 30% by weight. If the graphite content is less than 5% by weight, the resulting nozzle has poor spalling resistance, tending to develop a crack during preheating or in use. If the graphite content exceeds 30% by weight, the MgO layer formed on the hot surface through the reaction formulae (7) to (9) will have poor binding to the main body and will be liable to come off the main body, failing to perform the function as expected.

[0035] Furthermore, in cases where the spinel-periclase-graphite type refractories are applied to the portion around the spout of the nozzle for casting high-oxygen steel, high-Mn steel, Ca-treated steel, stainless steel, etc., the graphite content is preferably 5 to 20% by weight. If the graphite content is less than 5% by weight, the nozzle similarly has poor spalling resistance, tending to develop a crack during preheating or in use. If the graphite content is more than 20% by weight, the refractories will be damaged considerably due to dissolution of graphite into molten steel.

[0036] The periclase content in the spinel-periclase and spinel-periclase-graphite type refractories is desirably 40% by weight or smaller. Where the periclase content exceeds 40% by weight, the nozzle shows a tendency to slightly reduce the spalling resistance. If the periclase content exceeds 20% by weight or if the spinel content exceeds 95% by weight, the spalling resistance of the nozzle is deteriorated.

[0037] If the spinel content is less than 50% by weight, the proportions of periclase and graphite exceed the respective required ranges. It may follow that the MgO layer formed comes off the main body or the spalling resistance of the nozzle is deteriorated.

[0038] It is another important matter for the nozzle of the present invention that the refractory materials to be used have a controlled mineral composition. Components which are, while chemically analogous to each other, different in constituent mineral (crystal structure) show, of necessity, difference in reactivity to molten steel, which develops into a great difference in resistance against corrosion.

[0039] In the present invention, the refractories making the inner wall portion of the nozzle which comes into contact with molten steel may comprise spinel crystals, i.e., a composite oxide of  $\text{Al}_2\text{O}_3$  and MgO, or a combination of spinel crystals and periclase crystals comprising MgO.

[0040] It is desirable not to use an  $\text{Al}_2\text{O}_3$  component containing free  $\text{Al}_2\text{O}_3$  but to use a spinel ( $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ) raw material as an  $\text{Al}_2\text{O}_3$  component of the spinel-periclase or spinel-periclase-graphite type refractories. The spinel raw material to be used does not always need to have a theoretical  $\text{MgO}:\text{Al}_2\text{O}_3$  ratio and can include a material having excess MgO and comprising spinel and periclase or a material having excess  $\text{Al}_2\text{O}_3$  but containing no corundum as free alumina. Use of a raw material containing free  $\text{Al}_2\text{O}_3$  induces a reaction between the  $\text{Al}_2\text{O}_3$  and periclase inside the high temperature nozzle to form spinel, which tends to be accompanied by partial expansion or shrinkage in the nozzle, resulting in cracking.

[0041] The spinel raw materials and the magnesia raw materials can be either electrofused products or fired products.

[0042] Where practical refractory raw materials are used in the preparation of the spinel-periclase or spinel-periclase-graphite type refractories, the resulting refractories may unavoidably contain impurities. Such unavoidable impurities are preferably restricted to 3% by weight or less. If the impurities content exceeds 3% by weight, the reactions of formulae (7) to (9) are hindered from forming a dense MgO layer, and clogging or corrosion of the nozzle can result.

[0043] The submerged nozzle for continuous casting of steel of the present invention can be produced by, for example, as follows.

[0044] In cases where the spinel-periclase-graphite type refractories are used in the inner wall portion of a nozzle, the nozzle is produced by a method comprising simultaneously pressing a mixture of raw materials providing the spinel-periclase-graphite type refractories material which constitute the inner wall portion of the nozzle, a mixture of raw materials for the refractory material which constitutes the main body of the nozzle, and, if necessary, a mixture of raw materials for the spinel refractory material which constitutes at least a part of the inner wall portion other than the portion around the spout, to form a nozzle of prescribed shape (simultaneous forming method) or by a method comprising casting or injecting a kneaded mixture of raw materials providing the spinel-periclase-graphite type refractory material which constitutes the inner wall portion into a previously formed main body of the nozzle, followed by drying and if necessary, firing (insert forming method).

[0045] In carrying out the simultaneous forming, the raw material mixture kneaded with a binder, such as phenol resins or polysaccharides, for the refractory material of the present invention, or the raw material mixture kneaded with a binder for the refractory material constituting the nozzle main body, and the raw material mixture for the refractory material of the present invention which constitutes the inner wall portion are packed into the respective positions of a frame mold, formed by CIP, etc., and dried to give an unburned product. Or, the formed green body is fired to give a burned product.

[0046] It is recommended that the binder of the refractories constituting the main body and that of the refractories of the present invention which constitute the inner wall portion be the same.

[0047] In carrying out the insert forming method, the main body of the nozzle is previously prepared in a conven-

tional manner, and the raw material mixture kneaded with the same binder as used in the main body or such a binder as a silicate or a phosphate is cast or injected into the main body and dried, if desired, followed by firing.

[0048] A method comprising inserting an inner member which has previously been formed by pressing, casting or injection into the main body which has previously been formed in a conventional manner is unfavorable because the affinity (adhesion stability) between the inner member and the main body is poor. In order to maintain the adhesion stably when the nozzle is heated to high temperature in use, the above-described simultaneous forming or insert forming method are recommended because the above-described spinel-periclase-graphite type refractories of the present invention which constitutes the inner wall portion is more expansive than the  $\text{Al}_2\text{O}_3\text{-C}$  type refractories or AG-based refractories of the main body.

[0049] Similarly, it is preferred for the refractories of the main body and that of the inner wall portion be kneaded with the same binder to secure the affinity and to stabilize the adhesion.

[0050] It is preferred for the starting material mixture forming the refractories of the present invention to have a grain size of not greater than  $1000\ \mu\text{m}$  and to comprise particles having a grain size of  $500\ \mu\text{m}$  or smaller in a proportion of 60% by weight or more. If there are too many grains greater than  $1000\ \mu\text{m}$ , for example, if their proportion exceeds 20% by weight, these grains, too large for the wall thickness, cause embrittlement of the refractory structure and may fall off during use. If the proportion of grains of  $500\ \mu\text{m}$  or smaller is less than 60% by weight, cases are often met with in which the formability, particularly in simultaneous forming, is insufficient for obtaining a satisfactory formed body. Further, presence of more than 20% by weight of grains smaller than  $0.5\ \mu\text{m}$  is undesirable because the resulting refractories tend to have poor spalling resistance and develop cracks.

[0051] Where the inner wall portion is made of different refractories from that making the main nozzle body, the thickness of the inner wall portion preferably ranges from 1 to 10 mm. With the thickness of the inner wall portion being smaller than 1 mm, that part tends to be too weak to stand the impact of a molten steel flow and may fall off the main body. If the thickness exceeds 10 mm, there is a fear that the difference in thermal expansion from the refractories making the main nozzle body may be so large as to cause cracking (i. e., the spalling resistance is deteriorated).

[0052] Refractories having a conventional composition, such as  $\text{ZrO}_2\text{-C}$  type refractories may be used in the powder line portion of the main nozzle body.

[0053] The main nozzle body can be made of appropriate AG-based refractories materials and the like which have conventionally been used. The AG-based refractories materials include those of conventional compositions, for example, those comprising 30 to 90% by weight of  $\text{Al}_2\text{O}_3$ , 0 to 35% by weight of  $\text{SiO}_2$ , and 10 to 35% by weight of C.

[0054] The  $\text{ZrO}_2\text{-C}$  type refractories, for example,  $\text{CaO}$ -stabilized  $\text{ZrO}_2$ , include those comprising 66 to 88% by weight of  $\text{ZrO}_2$ , 2 to 4% by weight of  $\text{CaO}$ , and 10 to 30% by weight of C. Useful  $\text{ZrO}_2$  raw materials include  $\text{CaO}$ -stabilized  $\text{ZrO}_2$ , which are widely employed, and, in addition,  $\text{MgO}$ -stabilized  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$ , vaterite, and the like.

#### Brief Description of the Drawings:

##### [0055]

Fig. 1 shows a first embodiment of the nozzle according to the present invention (material arrangement pattern 1).

Fig. 2 shows a second embodiment of the nozzle according to the present invention (material arrangement pattern 2).

Fig. 3 shows a third embodiment of the nozzle according to the present invention (material arrangement pattern 3).

Fig. 4 shows a fourth embodiment of the nozzle according to the present invention (material arrangement pattern 4).

Fig. 5 shows a fifth embodiment of the nozzle according to the present invention (material arrangement pattern 5).

Fig. 6 shows a sixth embodiment of the nozzle according to the present invention (material arrangement pattern 6).

Fig. 7 shows a seventh embodiment of the nozzle according to the present invention (material arrangement pattern 7).

Fig. 8 shows an eighth embodiment of the nozzle according to the present invention (material arrangement pattern 8).

Fig. 9 is material arrangement pattern 9 of a conventional nozzle (Comparative Example 1).

Fig. 10 shows material arrangement pattern 10 of another conventional nozzle (Comparative Example 2).

Fig. 11 shows material arrangement pattern 11 of the nozzles of Comparative Examples 3 to 5.

Fig. 12 shows material arrangement pattern 12 of a conventional AG-based nozzle (Comparative Example 6).

#### Best Mode for Carrying out the Invention:

[0056] The present invention will be illustrated in detail with reference to the accompanying drawings, but the present invention is not construed as being limited to the following embodiments.

[First embodiment:]

[0057] Fig. 1 depicts the first embodiment of the nozzle of the present invention (material arrangement pattern 1), wherein 10 is the nozzle body totally made up of spinel-periclase-graphite type refractory (spinel: 50 to 95 wt%; periclase: 0 to 20 wt%; graphite: 5 to 30 wt%; unavoidable impurities: 3 wt% or less), and 11a indicates the inner wall of the nozzle body 10.

[Second embodiment:]

[0058] Fig. 2 illustrates the second embodiment of the nozzle of the present invention (material arrangement pattern 2), in which 10 is the main nozzle body made up of AG-based refractory; 1 is the inner wall portion made of the above-described spinel-periclase-graphite type refractory; 2 is the part of the inner wall portion 1 of the main nozzle body 10, which surrounds the spout; and 3 indicates a powder line portion made of  $ZrO_2$ -C type refractory.

[Third embodiment:]

[0059] Fig. 3 shows the third embodiment of the nozzle of the present invention (material arrangement pattern 3), in which 10 is the main nozzle body made up of AG-based refractory; 2 is the part of the inner wall portion which is around the spout and is made of the above-described spinel-periclase-graphite type refractory; and 3 indicates a powder line portion made of  $ZrO_2$ -C type refractory.

[Fourth embodiment:]

[0060] Fig. 4 represents the fourth embodiment of the nozzle of the present invention (material arrangement pattern 4), in which 10 is the main nozzle body made up of AG-based refractory; 1 is the inner wall portion made of the above-described spinel-periclase-graphite type refractory; and 3 indicates a powder line portion made of  $ZrO_2$ -C type refractory.

[0061] To make the present invention more clearly understandable, comparative material arrangement patterns are presented hereunder.

[0062] Fig. 9 and 10 show material arrangement patterns 9 and 10 which are different from material arrangement patterns 1 to 4 of the 1st to 4th embodiments of the nozzle according to the present invention, wherein 10 is the main body made of AG-based refractory; 13 is a powder line portion made of  $ZrO_2$ -C type refractory; and 11 is the inner wall portion made of high-purity alumina refractory.

[Fifth to seventh embodiments:]

[0063] Figs. 5 through 7 depict additional three embodiments (material arrangement patterns 5 to 7) of the nozzle according to the present invention, wherein 1 is the inner wall portion made up of the spinel-periclase type refractory of the present invention; 2 indicates the portion around the spout which is made of the spinel-periclase-C type refractory of the present invention; 10 is the main body made of AG-based refractory; and 3 is a powder line portion made of  $ZrO_2$ -C type refractory.

[Eighth embodiment:]

[0064] Fig. 8 is an illustration showing an embodiment of the nozzle according to the present invention (material arrangement pattern 8), wherein 10 indicates the main body made up of AG-based refractory; 1 indicates the inner wall portion made up of the refractory of the present invention, the spinel-periclase type refractory; 10a is the inner wall portion made of AG-based refractory; 2 is the portion around the spout made up of the refractory of the present invention, the spinel-periclase-C type refractory; and 3 is a powder line portion made of  $ZrO_2$ -C type refractory.

To make the present invention more clearly understandable, material arrangement patterns comparative to the above embodiments are presented hereunder.

[0066] Figs. 11 and 12 illustrate material arrangement patterns 11 and 12, which are different from the 5th to 7th embodiments of the present invention, wherein the inner wall portion 11 and the portion 12 around the spout are made up of the same refractory (unlike material arrangement patterns 5 to 7 wherein the inner wall portion 11 and the portion 12 around the spout are made of different refractory). Specifically, in material arrangement pattern 11 the inner wall portion 11 and the portion 12 around the spout are made of the spinel-periclase type refractory, and in material arrangement pattern 12 the inner wall portion 11 and the portion 12 around the spout are made of conventional AG-based refractory. Numeral 13 is a powder line portion made of  $ZrO_2$ -C type refractory.

[ Examples : ]

[0067] The present invention will now be illustrated in the concrete first with reference to Examples using the nozzles of the 1st to 4th embodiments in view of Comparative Examples.

[Examples 1 to 5:]

[0068] The material arrangement pattern shown in Fig. 2 was adopted. The powder line portion 3 was made of a  $ZrO_2$ -C type refractory material (CaO-stabilized  $ZrO$ : 80 wt%; graphite: 20 wt%), and the main nozzle body 10 was made of a commonly used AG-based refractory material ( $SiO_2$ : 25 wt%; C: 28 wt%;  $Al_2O_3$ : balance). The inner wall portion 1 was made of a spinel-periclase-graphite type refractory material, the formulation of which is shown in Table 1 below. The refractory material of the inner wall portion 1 was 8 mm thick.

TABLE 1

	Example 1	Example 2	Example 3	Example 4	Example 5
Spinel	88	82	85	69	72
Periclase	5	3	7	4	18
Graphite	7	15	15	27	10

[Comparative Example 1:]

[0069] Material arrangement pattern 9 shown in Fig. 9 was used. The powder line portion 13 was made of a  $ZrO_2$ -C type refractory material (CaO-stabilized  $ZrO$ : 80 wt%; graphite: 20 wt%), and the main nozzle body 10 was made of a commonly used AG-based refractory material ( $SiO_2$ : 25 wt%; C: 28 wt%;  $Al_2O_3$ : balance).

[Comparative Example 2:]

[0070] Material arrangement pattern 10 shown in Fig. 10 was used. The powder line portion 13 was made of a  $ZrO_2$ -C type refractory material (CaO-stabilized  $ZrO_2$ : 80 wt%; graphite: 20 wt%), the main nozzle body 10 was made of a commonly used AG-based refractory material ( $SiO_2$ : 25 wt%; C: 28 wt%;  $Al_2O_3$ : balance), and the inner wall portion 11 was made of high-purity  $Al_2O_3$  (thickness: 8 mm).

[0071] The effects of the nozzles according to the present invention were evaluated by testing in actual use.

[Test 1:]

[0072] The nozzles were tested in casting low-carbon Al-killed steel having a composition (wt%) of C: 0.08; Si: 0.03; Mn: 0.2; P: 0.01; S: 0.01; Al: 0.05; O: 0.003. Casting was conducted at a temperature of 1580°C for 250 minutes.

[0073] As a result of the test, the nozzles of Comparative Examples 1 and 2 were found to have formed an  $Al_2O_3$  deposition layer having a thickness of 12 mm or 15 mm, respectively, on the hot surface thereof, whereas the  $Al_2O_3$  deposition layer on the nozzles of Examples 1 to 5 was only 2 to 4 mm thick, revealing great effects in suppressing  $Al_2O_3$  deposition. The nozzles of Examples 1 and 5 suffered from no cracks nor fall-off in the inner wall portion thereof, enabling operation with safety. One out of four tested nozzles of Comparative Example 2 was broken in use.

[Test 2:]

[0074] The nozzles were tested in casting high-oxygen steel having a composition (wt%) of C: 0.003; Si: 0.002; Mn: 0.3; P: 0.01; S: 0.01; Al: 0.001 ppm; O: 0.06. Casting was conducted at a temperature of 1560°C for 230 minutes.

[0075] As a result of the test, the maximum damage thickness on the inner wall was 8 mm and 11 mm in the nozzles of Comparative Examples 1 and 2, respectively, whereas it was as small as 1 to 3 mm in the nozzles of Examples 1 to 5, proving that the corrosion of the nozzles was markedly small. In this test, too, the nozzles of Examples suffered from no cracks nor fall-off, securing safe operation.

[Test 3:]

[0076] The nozzles were tested in casting high-Mn steel having a composition (wt%) of C: 0.04; Si: 0.02; Mn: 1.5;



P: 0.01; S: 0.01; O: 0.01. As a result of 210 minute casting at 1560°C, the nozzles of Comparative Examples 1 and 2 showed a maximum damage thickness of 10 mm and 13 mm, respectively, on the inner wall thereof, whereas the maximum damage thickness in Examples 1 to 5 was as small as 1 to 4 mm, proving that the corrosion of the nozzles was markedly reduced. Further, the nozzles of Examples suffered from no cracks nor fall-off.

[Test 4:]

[0077] The nozzles were tested in casting stainless steel having a composition (wt%) of C: 0.05; Si: 0.5; Mn: 1.0; P: 0.04; S: 0.02; Ni: 8.0; Cr: 18.0; O: 0.005. As a result of 260 minute casting at a temperature of 1550°C, the nozzles of Comparative Examples 1 and 2 suffered a maximum damage thickness on the inner wall of 8 mm and 9 mm, respectively, whereas the maximum damage thickness in Examples 1 to 5 was as small as 0.5 to 2 mm, proving that the corrosion of the nozzles was greatly reduced. Further, the nozzles of Examples suffered from no cracks nor fall-off.

[Test 5:]

[0078] The nozzles were tested in casting stainless steel having a composition (wt%) of C: 0.05; Si: 0.3; Mn: 0.8; P: 0.01; S: 0.01; Al: 0.02; Ca: 0.003; O: 0.002. As a result of 200 minute casting at 1580°C, the nozzles of Comparative Examples 1 and 2 suffered a maximum damage thickness on the inner wall of 8 mm and 10 mm, respectively, whereas the maximum damage thickness in Examples 1 to 5 was as small as 2 mm each, proving that the corrosion of the nozzles was markedly reduced. Further, the nozzles of Examples suffered from no cracks nor fall-off.

[0079] In what follows Examples of using the nozzles of the 5th to 8th embodiments are shown together with Comparative Examples to describe the present invention in the concrete. Before going into these Examples, various Test Examples are shown.

[Test Examples:]

[0080] The raw materials shown in Table 2 which provided the mineral, phase shown were mixed up in the ratio shown. Samples 1 to 5 according to the present invention and comparative samples 1 to 6 were prepared by using the resulting mixtures and subjected to various evaluation tests.

#### 1. Corrosion resistance test

[0081] Samples 1 to 5 of the present invention and comparative samples 1 to 6 were dipped in molten steel to carry out a test for evaluating corrosion resistance.

[0082] High-oxygen steel was melted in a high frequency induction furnace in an argon atmosphere and maintained at 1580°C. A sample of 40 mm in diameter and 230 mm in height was dipped in the molten steel and rotated at 100 r.p.m. for 60 minutes. Then the corrosion was measured from the diameter of the sample and evaluated in terms of corrosion index, taking the corrosion of the AG-based refractory of the comparative sample as 1. The smaller the corrosion index, the higher the corrosion resistance. The same test was carried out with high-Mn steel, stainless steel, and Ca-treated steel. The results obtained are shown in Table 2.

TABLE 2

	Sample of Invention					Comparative Sample					
	1	2	3	4	5	1	2	3	4	5	6
Component (wt%):											
Al <sub>2</sub> O <sub>3</sub>	72	60	50	66	60	55	-	100	-	50	58
MgO	28	40	50	26	23	-	-	-	100	50	19
ZrO <sub>2</sub>	-	-	-	-	-	-	95*	-	-	-	-
SiO <sub>2</sub>	-	-	-	-	-	25	-	-	-	-	-
Graphite	-	-	-	8	17	20	-	-	-	-	23
Mineral Phase**	S	S, P	S, P	S, G	S, G	M, G	Z	C	P	C, P	S, C, G
Corrosion Index:											
High-oxygen steel	0.1	0.1	0.1	0.2	0.3	1	0.7	0.6	***	***	0.6
High-Mn steel	0.1	0.1	0.1	0.2	0.3	1	0.6	0.6	***	***	0.5
Stainless steel	0.1	0.1	0.1	0.2	0.2	1	0.5	0.7	***	***	0.6
Ca-treated steel	0.1	0.1	0.1	0.2	0.3	1	0.6	0.6	***	***	0.5

Note:

\*: Containing 5% of CaO

\*\* : S: spinel; P: periclase; M: mullite; Z: zirconia; C: corundum; G: graphite

\*\*\*: The sample developed cracks and fell off.

[0083] The above table reveals the following facts.

1) The spinel of sample 1 of the present invention and the (spinel + periclase) of samples 2 and 3 of the present invention showed very slight corrosion in any kind of molten steel.

2) Irrespective of the kind of molten steel, the AG-based refractory of comparative sample 1, which is commonly employed, exhibited the greatest corrosion. The degree of corrosion decreased in the order of ZrO<sub>2</sub> (comparative sample 2), Al<sub>2</sub>O<sub>3</sub> (comparative sample 3), and (Al<sub>2</sub>O<sub>3</sub>+MgO) (comparative sample 5). Although comparative samples 4 and 5 showed no appreciable corrosion, comparative sample 4 developed many cracks, and comparative sample 5 also suffered from cracks.

3) As for the influences of graphite content on corrosion, when present in a proportion of 20 wt% or more, graphite exerted considerable influences. As far as the graphite content is smaller than that, although the corrosion tendency increased with the graphite content, the corrosion observed was not so noticeable.

## 2. Spalling resistance test

[0084] Nozzles of the present invention were prepared by using the samples shown in Table 2 as a member constituting the inner wall portion or the portion around the spout. The spalling resistance of the resulting nozzles was evaluated.

[0085] Material arrangement pattern 5 shown in Fig. 5 was applied to the nozzles of the present invention, while material arrangement pattern 11 shown in Fig. 11 was used in the comparative nozzles. An AG-based refractory material comprising 55 wt% of Al<sub>2</sub>O<sub>3</sub>, 25 wt% of SiO<sub>2</sub>, and 20 wt% of C was used as the nozzle main body in each sample.

[0086] Each of the nozzles was immersed in 100 kg of molten steel for 60 seconds, pulled up, and air-cooled. Crack development was examined. The results are shown in Table 3.

TABLE 3

		Example			Comparative Example				
		6	7	8	3	4	5	6	
Disposition of Material	Inner wall portion	sample 1 of invention in Table 2	sample 2 of invention in Table 2	sample 3 of invention in Table 2	sample 1 of invention in Table 2	sample 2 of invention in Table 2	sample 3 of invention in Table 2	comparative sample 1 in Table 2	
	portion around spout	sample 4 of invention in Table 2	sample 4 of invention in Table 2	sample 4 of invention in Table 2	do.	do.	do.	do.	
	pattern	Fig. 5	Fig. 5	Fig. 5	Fig. 11	Fig. 11	Fig. 11	Fig. 12	
	Crack development	not observed	not observed	not observed	observed	observed	observed	observed	

[Examples 6 to 8 and Comparative Examples 3 to 5:]

[0087] In Examples 6 to 8 according to the present invention, various submerged nozzles for continuous casting were obtained by disposing samples 1 to 3 of the invention in the inner wall portion and sample 4 of the invention in the portion around the spout as shown in Table 3 according to the material arrangement pattern shown in Fig. 5.

[0088] In Comparative Examples 3 to 5 various comparative nozzles for continuous casting were obtained by applying samples 1 to 3 of the invention to both the inner wall portion and the portion around the spout as shown in Table 3 according to material arrangement pattern 11 shown in Fig. 11.

[0089] In Comparative Example 6 a conventional AG-based nozzle having material arrangement pattern 12 shown in Fig. 12 was obtained by applying comparative sample 1 to both the inner wall portion and the portion around the spout as shown in Table 3.

[0090] The nozzle of the present invention and the comparative nozzle were tested in actual use for continuous casting of high-oxygen steel, high-Mn steel, stainless steel and Ca-treated steel.

i) Use as submerged nozzle for continuous casting of high-oxygen steel

[0091] The submerged nozzle of Example 6 and the AG-based nozzle of Comparative Example 6 were tested in continuous casting of high-oxygen steel having a composition (wt%) of C: 30 ppm; Si: 20 ppm; Mn: 0.3; P: 0.01; S: 0.01; Al: 10 ppm; O: 0.06 ppm.

[0092] As a result of the test, the maximum damage thickness of the inner wall after 230 minute casting was 12 mm in the nozzle of Comparative Example 6, while it was as small as 2 mm in the nozzle of Example 6, demonstrating remarkable reduction in nozzle corrosion. The nozzle of Example 6 suffered from neither cracks nor fall-off in the inner wall portion thereof, enabling operation with safety.

ii) Use as submerged nozzle for continuous casting of high-Mn steel

[0093] The two submerged nozzles as tested in (i) above were used in continuous casting of high-Mn steel having a composition of C: 0.04; Si: 0.02; Mn: 1.5; P: 0.01; S: 0.01; O: 100 ppm.

[0094] As a result of 210 minute casting, the maximum damage thickness of the inner wall portion was 13 mm in the nozzle of Comparative Example 6, while it was as small as 2.5 mm in the nozzle of Example 6, showing remarkable reduction in corrosion of the nozzle. The nozzle of Example 6 suffered from neither cracks nor fall-off in the inner wall portion thereof.

iii) Use as submerged nozzle for continuous casting of stainless steel

[0095] The two submerged nozzles as tested in (i) above were used in continuous casting of stainless steel having a composition (wt%) of C: 0.05; Si: 0.5; Mn: 1.0; P: 0.04; S: 0.02; Ni: 8.0; Cr: 18.0; O: 50 ppm.

[0096] As a result of the test, the maximum damage thickness of the inner wall portion after 260 minute casting was 9 mm in the nozzle of Comparative Example 6, and that of the nozzle of Example 6 was 1 mm, showing a great reduction in nozzle corrosion. Further, the nozzle of Example 6 suffered from neither cracks nor fall-off in the inner wall portion thereof. iv) Use as submerged nozzle for continuous casting of Ca-treated steel

[0097] The two submerged nozzles as tested in (i) above were used in continuous casting of Ca-treated steel having a composition (wt%) of C: 0.05; Si: 0.3; Mn: 0.8; P: 0.01; S: 0.01; Al: 0.02; Ca: 30 ppm; O: 20 ppm.

[0098] As a result of the test, the maximum damage thickness of the inner wall portion after 200 minute casting was 8 mm in the nozzle of Comparative Example 6, while it was 1 mm in the nozzle of Example 6, showing a great reduction in nozzle corrosion. Further, the nozzle of Example 6 suffered from neither cracks nor fall-off in the inner wall portion thereof.

[0099] The results in Table 3 reveals that the nozzle of the present invention having the spinel-periclase-C type refractory material in the portion around the spout developed no cracks in every test, whereas the comparative nozzle containing no graphite in the portion around the spout developed cracks in the vicinities of the spout in every test.

Industrial Applicability:

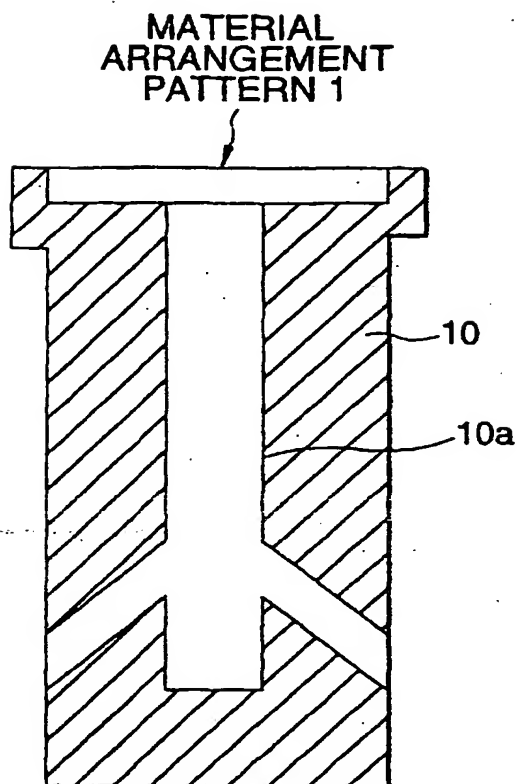
[0100] As described above in detail, in the submerged nozzle for continuous casting of steel according to the present invention, since the whole nozzle or a part of the inner wall portion thereof which comes into contact with molten steel comprises a spinel-periclase-C type refractory material, particularly a spinel-periclase-graphite type refractory material comprising 50 to 95% by weight of spinel, 0 to 20% by weight of periclase, 5 to 30% by weight of graphite, and not more than 3% by weight of unavoidable impurities, clogging of the nozzle due to deposition of  $Al_2O_3$  contained in

steel is greatly suppressed, corrosion of the nozzle is markedly reduced, and there is no fear of the nozzle cracking, securing safety in operation. Therefore, the nozzle of the present invention is suitable to not only casting of Al-killed steel but casting of high-oxygen steel, high-Mn steel, Ca-treated steel, stainless steel, etc.

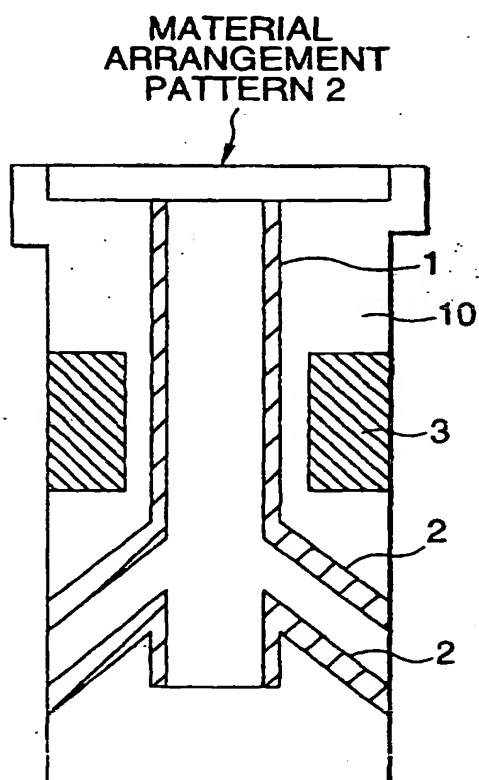
## 5 Claims

1. A submerged nozzle for continuous casting of steel characterized in that the whole nozzle or a part or the whole of the inner wall portion thereof which comes into contact with molten steel is made of a spinel-periclase-graphite type refractory material.
2. A submerged nozzle for continuous casting of steel according to claim 1, which is characterized in that said spinel-periclase-graphite type refractory material comprises 50 to 95% by weight of spinel, 0 to 20% by weight periclase, 5 to 30% by weight of graphite, and not more than 3% by weight of unavoidable impurities.
3. A submerged nozzle for continuous casting of steel according to claim 1 or 2, which is characterized in that at least a part of the inner wall portion of the nozzle which comes into contact with molten steel is made of said spinel-periclase type refractory material, and at least a part of the portion surrounding the spout is made of said spinel-periclase-graphite type refractory material.
4. A submerged nozzle for continuous casting of steel according to claim 3, which is characterized in that at least a part of the inner wall portion of the nozzle which comes into contact with molten steel is made of said spinel-periclase type refractory material, and at least a part of the portion surrounding the spout is made of said spinel-periclase-graphite type refractory material which has a graphite content of 5 to 20% by weight.

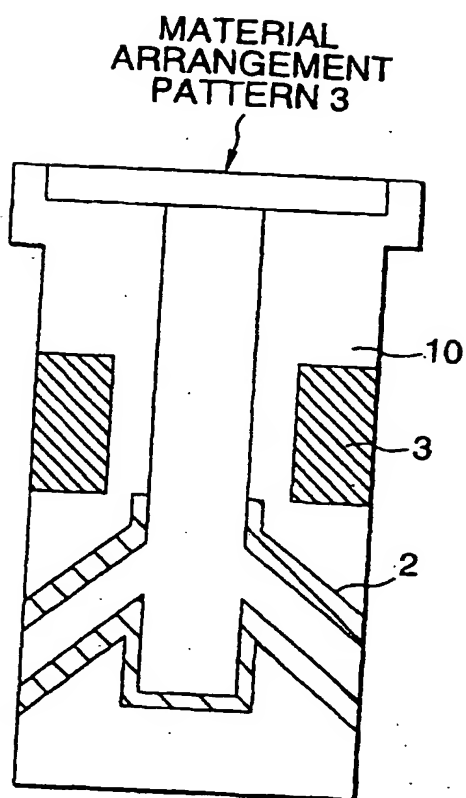
**FIG. 1**



**FIG. 2**



**FIG. 3**



**FIG. 4**

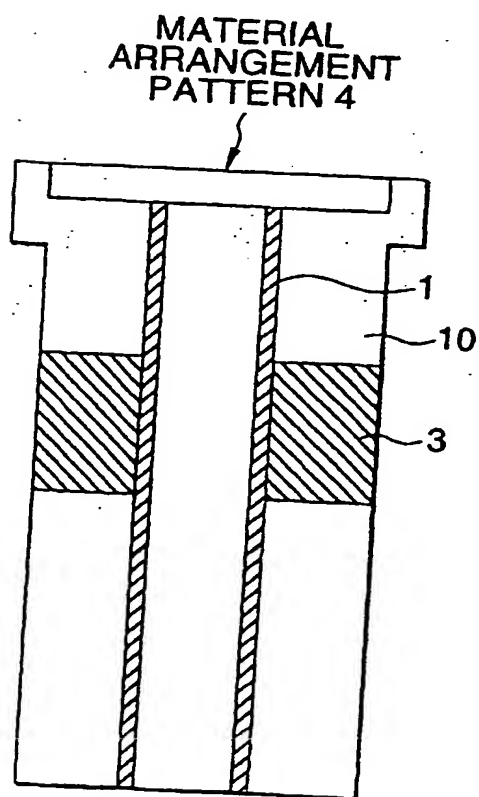


FIG. 5

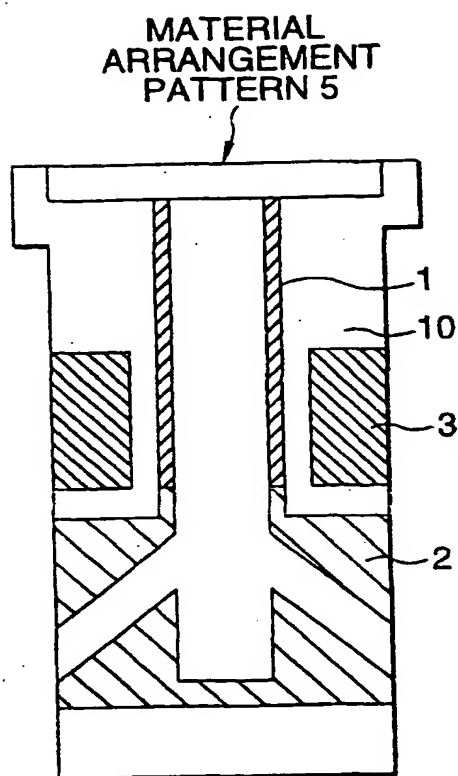


FIG. 6

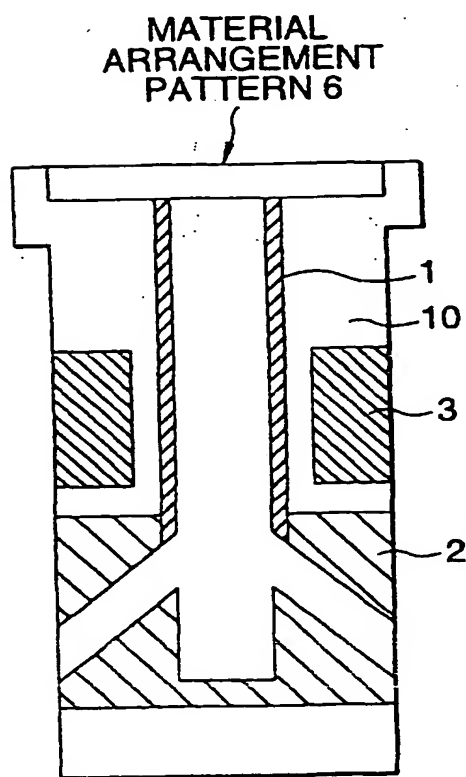




FIG. 7

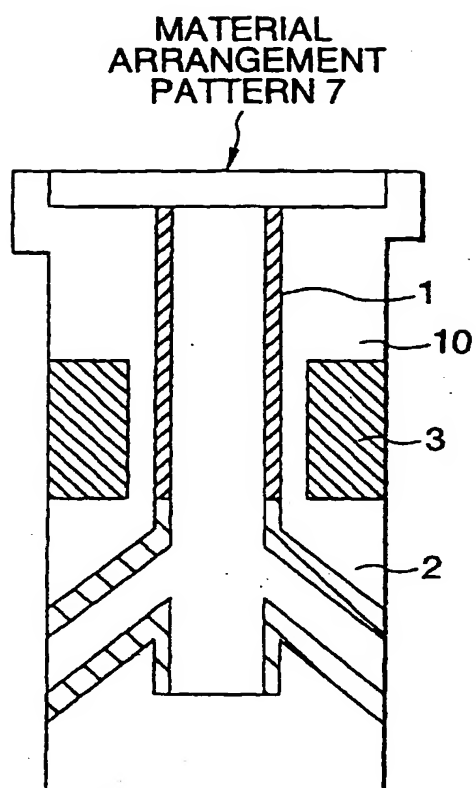
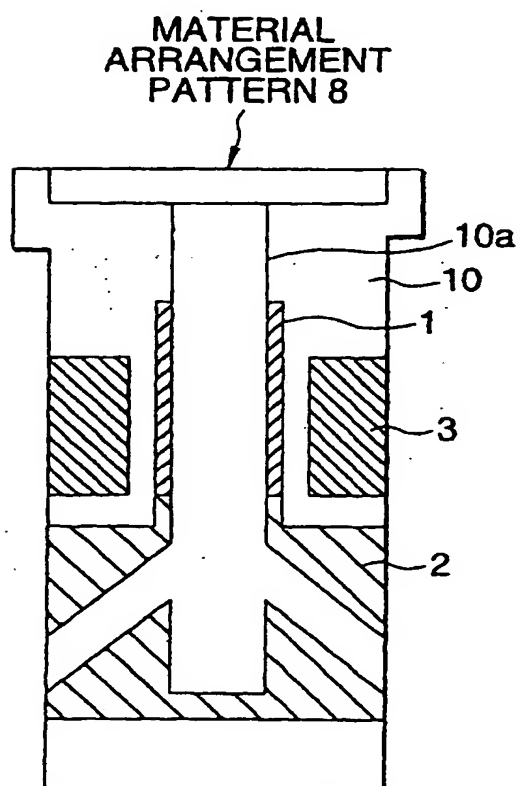
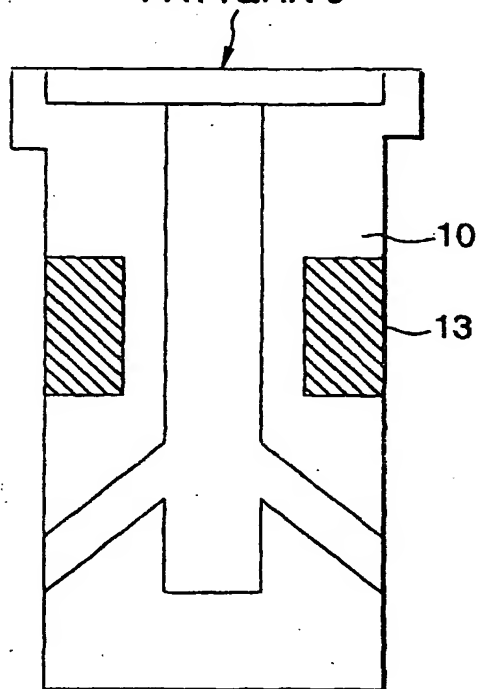


FIG. 8



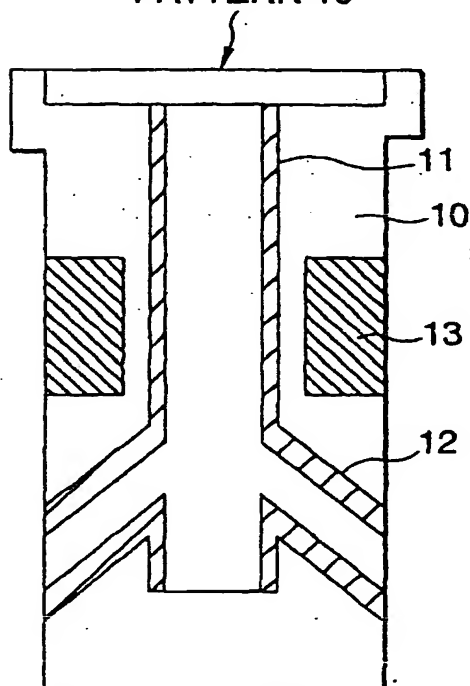
**FIG. 9**

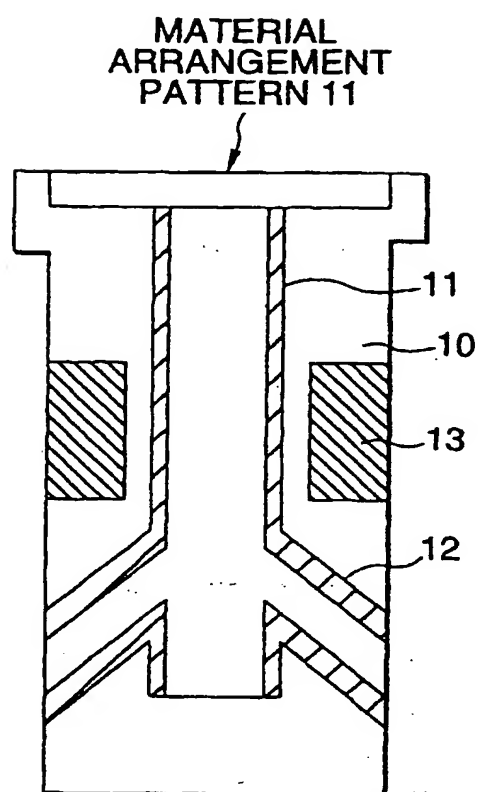
MATERIAL  
ARRANGEMENT  
PATTERN 9



**FIG. 10**

MATERIAL  
ARRANGEMENT  
PATTERN 10



**FIG. 11****FIG. 12**